

An Investigation of Mesocyclic and Acyclic Dithioether Cation Radicals and Dications

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Abstract: The one- and two-electron oxidation of a series of mesocyclic and acyclic dithioethers is reported. A long-lived cation radical is formed in solution when either 1,5-dithiacyclooctane (1,5-DTCO) or 1,5-dithiacyclononane (1,5-DTCN) is oxidized with 1 equiv of NO^+ . No radicals are observed when other dithioethers are oxidized under similar conditions. These are the first long-lived, nonaromatic sulfur-containing radicals reported. The ESR spectrum of the 1,5-DTCO cation radical is consistent with a structure having a sulfur-sulfur bond with the free electron localized on only one sulfur, although other interpretations are possible. Oxidation of 1,5-DTCO with NOPF_6 in propionitrile results in a red solid which gives the correct elemental analysis for $(1,5\text{-DTCO})\text{PF}_6$ but it appears to be a dimer. Dithioether dications are formed when 2 equiv of the oxidizing agent are consumed as evidenced by the evolution of NO. In the eight-, nine-, and ten-membered ring dithioethers, when the two sulfur atoms are separated by three or four methylene groups, oxidation gives solid dithioether dications which are characterized by elemental analysis and ^{13}C NMR. Although other mesocyclic and acyclic dithioethers, which have from two to four methylene groups between sulfur atoms, undergo a two-electron oxidation, dications were not isolated in the solid state. Nevertheless, all the dithioether dications formed in solution were converted to dithioether monosulfoxides in high yield with aqueous bicarbonate to confirm the identity of the dications. Other reactions of the 1,5-DTCO dication include oxidation of iodide, oxidation of alcohols, and reaction with 1,5-DTCO itself to give the 1,5-DTCO cation radical. Preliminary electrochemical results indicate facile oxidation of mesocyclic dithioethers.

Introduction

It is well known that aliphatic thioethers are oxidized to sulfoxides and sulfones with oxygen transfer agents (hydrogen peroxide, sodium periodate, *m*-chloroperbenzoic acid, etc.) by a two-electron process. However, only recently has it been shown that aliphatic dithioethers can be oxidized by successive one-electron steps to give long-lived radicals¹ and dications.²

In 1969, Cottrell and Mann measured the oxidation potential of a series of commercially available thioethers and thiols in acetonitrile and studied the anodic oxidation of dimethyl sulfide in detail. The overall reaction was suggested to involve a series of electrochemical and chemical steps in which dimethyl sulfide is oxidized to a transient cation radical in the first step. The characterized product is a thiomethylmethyl dimethylsulfonium salt.³

Norman and co-workers oxidized various monothioethers, such as dimethyl sulfide and tetrahydrothiophene, with titanium(III)-hydrogen peroxide in aqueous solution in an ESR flow system. They reported that the initially formed cation radical reacts rapidly with a molecule of neutral thioether to form a dimeric cation radical $[\text{R}_2\text{SSR}_2]^+$. Although one dithioether, 2,6-dithiaheptane (2,6-DTHP), was also examined, the ESR spectrum could not be attributed either to a dimeric cation radical or to a cyclic cation radical.⁴

Asmus and co-workers studied the oxidation of thioethers and disulfides with hydroxyl radicals generated by pulse radiolysis in aqueous solution.⁵ To account for the conductivity and the visible and ultraviolet absorptions, an intermediate OH-bridged neutral thioether dimer was proposed to form rapidly. Loss of hydroxide ion gives a dimeric cation radical identical with that proposed by Norman. Asmus also found that when the dithioether, 1,4-dithiane (1,4-DT), is oxidized, two different species form depending on the concentration. At concentrations of 1,4-DT greater than 10^{-3} M, the visible spectrum shows a λ_{max} near 500 nm, which is typical for dimeric cation radicals. At lower concentrations the λ_{max} is at 660 nm. The compound which gives this latter absorption is thought to be the 1,4-dithiane cation radical with an intramolecular S-S bond.⁶

There are examples of cation radicals between two heteroatoms other than sulfur. Ever since the ESR spectrum of the

cation radical of tetramethylhydrazine was observed, substituted hydrazines have been studied to determine the effect of various nitrogen substituents on the stability of the radical. Nelsen and co-workers studied the cyclic voltammetry,^{7a} photoelectron spectra (PES),^{7b} and NMR spectra^{7c} of several hydrazines and the ESR spectra^{7d} of their corresponding cation radicals in an effort to determine the stereochemistry about the nitrogen atoms. A long-lived hydrazine cation radical has been prepared by nitrosyl tetrafluoroborate oxidation of a hydrazine in which the two nitrogen atoms each bridge an eight-membered ring. The unpaired electron is thought to be in a π^* orbital. The presence of a dicationic species was observed by cyclic voltammetry.⁸ In a similar system in which an eight-membered ring diamine is fused to a perinaphthalene group, Alder and co-workers found that a one-electron oxidation gives a cation radical with a nitrogen-nitrogen σ bond.⁹ In this case the unpaired electron is thought to be in a σ^* orbital. Further oxidation gives a stable hydrazinium dication.⁹ A mesocyclic tertiary diamine, 1,5-dimethyl-1,5-diazacyclooctane, is oxidized rapidly by ferricyanide to give a transient red-colored solution which may be attributed to a cation radical. However, no ESR spectrum could be obtained.¹⁰

We previously reported that the oxidation of a mesocyclic dithioether, 1,5-dithiacyclooctane (1,5-DTCO), with a one-electron oxidizing agent, nitrosyl tetrafluoroborate, in acetonitrile gives both a cation radical¹ and a dication² depending on the stoichiometry. This was the first reported example of a solid dication containing a sulfur-sulfur bond.¹¹

To determine the scope of this reaction, a series of cyclic and acyclic dithioethers was examined. Only the symmetrical eight- and nine-membered ring dithioethers have the correct stereochemical requirements needed to give both cation radicals and dications which can be isolated and characterized. With smaller (six or seven) and larger (ten) membered rings only dications are observed. Likewise, in acyclic compounds with two to four methylenes bridging the thioether groups only dications are observed. Since many of the dications could not be isolated as stable solids, they were characterized by reaction with water to form monosulfoxides. However, since there were no reports of a general synthesis of monosulfoxides of dithioethers, a separate study of the synthesis of these monosulfoxides was undertaken.¹²

Figure 1 shows the dithioethers which were studied along with their names and abbreviations. Since the structures of the dithioethers are clearly suggested by the abbreviations, they will be used throughout.

Results and Discussion

Dithioether Cation Radicals. During the study of the oxidation of thioethers by copper(II), we noted that 1,5-DTCO reduces copper(II) extremely rapidly. Later it was found that 1,5-DTCO reacts with anhydrous tetrakis(acetonitrile)copper(II) tetrafluoroborate in dry acetonitrile in a ratio of 3:1 to give a yellow solution with λ_{\max} at 420 nm. This solution also gives an ESR spectrum with $g = 2.012$. The ESR signal is not a copper(II) signal but can be attributed to an organic radical.

The oxidation of 1,5-DTCO was investigated further using several nonmetal oxidizing agents such as nitrosyl tetrafluoroborate, nitrosyl hexafluorophosphate, and thianthrene tetrafluoroborate. The main advantage of using nitrosyl ion (NO^+) as an oxidizing agent is that the reduction product is nitric oxide, a gas. The nitric oxide can either be removed from the reaction by flushing with dry argon or nitrogen, or mea-



sured on a vacuum line as an indication of the extent of reaction. Normally 1,5-DTCO is added to nitrosyl tetrafluoroborate or nitrosyl hexafluorophosphate on a vacuum line and the nitric oxide is measured as it evolves. When 95% or more of the expected nitric oxide has been evolved, the reaction is stopped.

Both Norman⁴ and Asmus⁵ had suggested that dimeric cation radicals result from the oxidation of thioethers. In 1,5-DTCO there are two thioether groups in proximity to each other. Therefore, when one electron is removed and a positive charge develops on sulfur, a transannular interaction should occur between the two sulfur atoms. If the free electron of the cation radical were rapidly interconverting between the two sulfur atoms, a nine-line ESR spectrum, due to splitting by eight equivalent hydrogens on the α carbons, would be expected. However, the ESR spectrum obtained for 1,5-DTCO cation radical in solution is not a simple nine-line spectrum. Low-temperature ESR studies resolve the spectrum into a triplet of triplets with coupling constants of 15.4 and 10.2 G.¹ The computer-simulated spectrum is in good agreement with the actual spectrum. A possible structure for the 1,5-DTCO cation radical, which is consistent with this ESR spectrum, has the free electron localized on one sulfur atom. Thus the two sulfur atoms would be nonequivalent; one would be tetrahedral and the other trigonal bipyramidal. The four β hydrogens adjacent to the trigonal bipyramidal sulfur would be divided into two nonequivalent sets, and the electron would interact with each set in a different manner to give two triplets.¹ An alternative representation of the structure of the cation radical with the unpaired electron in a σ^* orbital could be invoked if the coupling of the free electron with four of the hydrogens happens to be very small and the other four electrons comprise two nonequivalent sets. The cation radical, (1,5-DTCO)BF₄, cannot be isolated as a solid, but an acetonitrile solution of the radical is stable for several days. However, by treating 1,5-DTCO with NOPF₆ in propionitrile at concentrations greater than 0.2 M, a red solid, which has the correct stoichiometry for the cation radical, is isolated. The solid exhibits an ESR spectrum which is similar to that observed for the cation radical in solution. Unfortunately, a magnetic susceptibility study indicates that the red solid is diamagnetic. Therefore, the ESR signal of the solid is probably due to trace amounts of 1,5-DTCO cation radical trapped in the solid. When the red solid is redissolved in propionitrile, the color of the solution turns

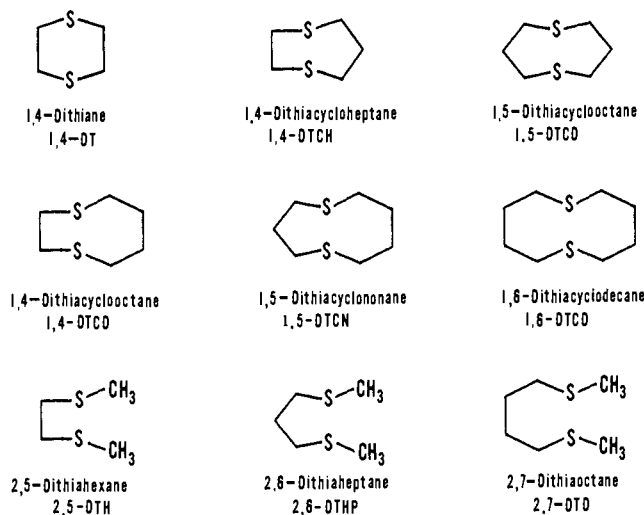


Figure 1. Structures and abbreviations for the dithioethers.

yellow and the ESR signal observed is identical with that of the cation radical. This behavior is similar to that of the elemental sulfur cation radical, S_8^+ . This cation radical also forms a diamagnetic red solid which apparently contains an S_{16}^{2+} dication. The structure of S_{16}^{2+} is not known, but it may contain intermolecularly fused S_8^+ units.^{1,3}

The only other dithioether to form a cation radical under these conditions is 1,5-DTCN. Like 1,5-DTCO cation radical, 1,5-DTCN cation radical is yellow colored in acetonitrile with a maximum absorbance at 420 nm. However, 1,5-DTCN cation radical is less stable than 1,5-DTCO cation radical and decays in a few hours at room temperature. When nitrosyl hexafluorophosphate is used to oxidize 1,5-DTCN, no solid is obtained. The ESR spectrum of 1,5-DTCN cation radical is more complex than that of 1,5-DTCO cation radical. If the free electron is localized in the same way as is postulated for 1,5-DTCO cation radical, there would be four nonequivalent β hydrogens and a complex ESR spectrum would be expected.

Although the other dithioethers undergo oxidation when 1 equiv of nitrosyl ion is added, no cation radicals are observed. When 1,4-DTCH or 1,4-DTCO is reacted with 1 equiv of nitrosyl ion, the solution changes in color from brown to yellow. Reaction of 1,6-DTCO with 1 equiv of nitrosyl ion results in an initial yellow solution which becomes clear and colorless when all the nitric oxide is evolved. Both 1,4-DT and 2,5-DTH react very slowly with nitrosyl ion. Initially the solution is deep red-brown and the color changes slowly through red and orange to yellow. Reaction of 2,6-DTHP and 2,7-DTO with 1 equiv of nitrosyl ion results in a blue-green solution that becomes yellow and then colorless as the nitric oxide is evolved. In an effort to identify the final products, the reaction was stopped when greater than 90% of the nitric oxide had been evolved, and the solvent was evaporated to give a sticky, oily residue, usually yellow to brown in color. In all cases the ¹³C NMR spectrum of the residue consists of a large number of peaks and no reasonable structure(s) can be proposed.

Dithioether Dications. We had hoped that the formation of the 1,5-DTCO cation radical could be followed by examining the increase in intensity of the 420-nm band in the visible spectrum with concomitant increase in the ESR signal. Neither oxidizing agent examined so far could be used for this study. As already mentioned, the cation radical of 1,5-DTCO could be formed using tetrakis(acetonitrile)copper(II) tetrafluoroborate as the oxidant in a ratio of 1,5-DTCO to copper of 3:1. At ratios less than 3:1, the observed ESR and the visible spectra are apparently due to complexes of copper and 1,5-DTCO of unknown stoichiometry. The main difficulty with NOBF₄ is

Table I

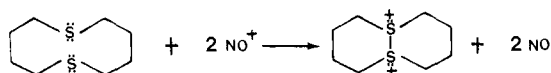
A. ^{13}C NMR of 1,5-DTCO, ^a 1,5-DTCN, ^a 1,6-DTCD, ^a and Their Dications ^b				
	ppm		ppm	
	C2 30.6 ^c		C2 53.0 ^c	
1,5-DTCO	C3 30.0	1,5-DTCO ²⁺	C3 35.0	
	C2 32.2 ^c		C2 51.4 ^c	
1,5-DTCN	C3 28.9	1,5-DTCN ²⁺	C3 33.5	
	C6 26.0 ^c		C6 34.5 ^c	
	C7 21.8 ^c		C7 14.4 ^c	
	C2 31.2		C2 36.7 ^d	
1,6-DTCD	C3 25.4	1,6-DTCD ²⁺	C3 16.8	
B. ^{13}C NMR of Bicyclic Sulfonium Salts ^b				
	cis		trans	
	C2 30.7 ^c	38.3 ^c		C2 46.6 ^c
	C3 20.0 ^c	23.9 ^c		C3 29.6 ^c
	C4 19.9 ^c	23.5 ^c		C4 36.2 ^c
	C5 26.1 ^c	30.7 ^c		C5 65.7
	C6 42.6	53.3		
C. ^{13}C NMR of 2,7-DTO ²⁺				
	C1 41.3 ^d			
	C3 23.8 ^d			
	C4 21.6 ^d			

^a Spectra were taken in CD_3CN ; parts per million relative to Me_4Si .

^b Spectra were taken in CDCl_3 ; parts per million relative to Me_4Si .
^c Double intensity. ^d Assignment based on off-resonance decoupling.

that the nitric oxide, which is evolved during the reaction, causes bubbling in the solution, thus making it difficult to obtain the spectra. Shine and co-workers have studied the chemistry of thianthrene cation radical extensively,¹¹ and it was thought that addition of 1,5-DTCO to thianthrene cation radical would cause a decrease in the thianthrene cation radical absorption at 546 nm and an increase of the 1,5-DTCO cation radical absorption at 420 nm. However, when approximately 0.5 equiv of 1,5-DTCO was added to a solution of thianthrene tetrafluoroborate, the resulting solution was clear and colorless with no visible absorption or ESR signal. At first it was thought that the solution had come into contact with air and the radical had decomposed. However, on addition of the other 0.5 equiv of 1,5-DTCO, a yellow solution with λ_{max} at 420 nm and the ESR signal which is characteristic of 1,5-DTCO cation radical was observed. This was the first indication that 1,5-DTCO could be oxidized to a dication and that the reaction of 1,5-DTCO dication with 1,5-DTCO gives the cation radical. Subsequently it was found that the dication is conveniently prepared by reacting 2 equiv of nitrosyl tetrafluoroborate with 1,5-DTCO on the vacuum line in acetonitrile. Fractional crystallization or addition of ether to this solution results in a colorless solid, which gives the correct elemental analysis for 1,5-DTCO(BF_4)₂.

The other mesocyclic dithioethers were treated with 2 equiv of nitrosyl tetrafluoroborate in the same manner as for 1,5-DTCO and, although all of the dithioethers undergo a two-electron oxidation and 80–90% of the expected nitric oxide is evolved, only 1,5-DTCN and 1,6-DTCD yield solid, colorless dications, which give the correct elemental analysis. Each of these three dithioether dications is believed to possess a sulfur–sulfur bond. These dications are therefore dialkylated



disulfides and represent a new functional group, as disulfides cannot be dialkylated by any known procedures.¹⁴ The stability of these dications is unusual considering that adjacent atoms are positively charged.

The ^1H NMR spectra of the dications are difficult to interpret because of complex multiplets from δ 2 to 4 which overlap each other. The ^{13}C NMR spectra of the dications are less complex, and the resonance of the various carbon atoms can be assigned (Table IA). Since these dications are the first and only dialkylated disulfides, there are no available data for comparison. There are data available for the cis- and trans-fused 1-thioniabicyclo[4.4.0]decane salts,¹⁵ as well as for the cis-fused 1-thioniabicyclo[3.3.0]octane¹⁶ (Table IB). Although these compounds are sulfonium salts, they are lacking in the sulfur–sulfur bond which is characteristic of the dications. It was thought at first that some information about the ring fusion could be obtained by a comparison of the ^{13}C data. In the cis-fused 1-thioniabicyclo[4.4.0]decane salt, the nonbridgehead carbon α to the cationic sulfur occurs at 30.7 ppm, while in the corresponding trans-fused system this α carbon is at 38.3 ppm. In the 1,6-DTCD dication, the α carbon is at 36.7 ppm, which is closer to the value of the trans-fused system. A trans-fused system is expected since the bicyclic six–six ring fused hydrazine is known to have a trans ring fusion,¹⁷ and *trans*-decalin is more stable than *cis*-decalin.¹⁸ The 1-thioniabicyclo[3.3.0]octane salt is thought to have cis-fused rings based on the carbocyclic system, and the nonbridgehead carbon α to the cationic sulfur occurs at 46.6 ppm. The α carbon in 1,5-DTCO dication occurs at 53.0 ppm, which is a difference of about 7 ppm. While this is not a large difference, it is approximately the same as the difference between the α carbons in the cis- and trans-fused 1-thioniabicyclo[4.4.0]decane salts. However, a cis ring fusion may also be expected here because the bicyclic five–five ring-fused hydrazine has a cis ring fusion,¹⁷ and from X-ray data the elemental sulfur dication has a cis ring fusion as well.¹⁹

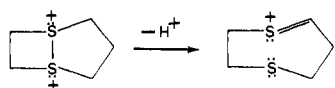
While these comparisons may at first appear to be useful, an examination of the ^{13}C data for the 1,5-DTCN dication makes them invalid. In 1,5-DTCN dication, a five-membered ring is fused to a six-membered ring. The carbons in the five-membered ring absorb at approximately the same frequency as those in the five-membered ring of the 1,5-DTCO dication. Likewise, the carbons in the six-membered ring of 1,5-DTCN dication absorb at the same frequency as those in the six-membered ring of 1,5-DTCD dication. Thus the ^{13}C data for the dications appear to be consistent within the ring systems and do not necessarily indicate whether the rings are fused in a cis or a trans fashion.

Transannular interactions in compounds where the two ring atoms are separated by a dimethylene chain should be rather weak and we did not anticipate that ring-fused bicyclic compounds with sulfur–sulfur bond would be formed in the oxidation of 1,4-DT, 1,4-DTCH, and 1,4-DTCO. The oxidation proceeds slower than that of the other mesocycles and solid dications could not be isolated. Nevertheless, the reactivity of these dications in solution suggests that they are bicyclic compounds which contain a four-membered ring.

In the acyclic dithioethers the two sulfur atoms are not held in proximity to each other and there is free rotation about both the carbon–carbon bonds and carbon–sulfur bonds. The two sulfur atoms can only interact when conformational changes cause them to be near each other so that a through-space interaction can occur. Such an interaction in 2,6-DTHP or 2,7-DTO would result in a five- or six-membered ring, respectively. When 2,7-DTO is reacted with 2 equiv of nitrosyl hexafluorophosphate in propionitrile at a concentration of 0.12 M, 90% of the nitric oxide is evolved and the solution becomes clear and colorless. The solvent is removed under vacuum and the residue is dried. The ^{13}C NMR spectrum of the residue

dissolved in CD_3CN gives three peaks, which is consistent with the formation of a six-membered ring dithioether dication (Table IC). Although a similar cyclic dication is expected in the oxidation of 2,6-DTHP, the ^{13}C NMR spectrum is complex. Therefore, in solution, the five-membered ring appears to be less stable than the six-membered ring. When the two sulfur atoms in 2,5-DTH interact intramolecularly, a four-membered ring would be formed and it is unlikely that the solid would be stable. The formation of intramolecular dications in the acyclic dithioethers, and perhaps in certain cyclic dithioethers as well, may depend on the concentration of the solution as noted by Asmus for 1,4-DT.⁶ In dilute solution an intramolecular interaction would be favored, whereas in a more concentrated solution an interaction between sulfur atoms of different molecules would be favored and polymer formation would occur.

Although all the dithioether dications decompose in solution, those having four-membered rings decompose more rapidly than those having larger rings. A possible decomposition route which relieves ring strain involves proton loss from an α carbon.



Because of their instability in solution, the dications are either isolated rapidly and stored as solids or used in a reaction as soon as they are formed. The reaction of the dication with the original dithioether was one of the first experiments carried out. When 1,5-DTCO dication is added to an equal molar amount of 1,5-DTCO, a yellow solution is obtained with a λ_{max} at 420 nm and an ESR spectrum identical with that of 1,5-DTCO cation radical. The same reaction is observed when 1,5-DTCN dication reacts with 1,5-DTCN. When 1,6-DTCD dication and 1,6-DTCD are mixed, no reaction occurs. Only a clear, colorless solution which does not exhibit an ESR signal is obtained. These results are in agreement with the one-electron oxidation of the dithioethers; only 1,5-DTCO and 1,5-DTCN form cation radicals.

Since the dication was a new functional group, its reactivity with various reagents was studied. Our prime concern was to find a reagent which would react to give high yields of a characterizable product. 1,5-DTCO dication was chosen as a model compound and was found to react either as an oxidizing agent or as an electrophile depending upon the added reagent. When tetra-*n*-butylammonium iodide is added to a solution of the dication, the solution immediately becomes the color of iodine. The dication also behaves as an oxidizing agent in oxidizing alcohols to aldehydes or ketones. Addition of isopropyl alcohol to the dication results in the formation of acetone. However, there are several problems encountered in the reaction of the dication with isopropyl alcohol. Only a 50% yield of acetone is obtained as determined by gas chromatography. In the reaction 2 equiv of protons are produced, and the solution becomes strongly acidic. The acid could be causing polymerization of acetone and account for the low yield. However, it is also possible that the low yield is due to a reaction of 1,5-DTCO dication with acetone. This reaction could proceed by the same route as the reaction of the perchlorate salt of 1,5-DTCO monosulfoxide with methyl ketones to give sulfonium salts.²⁰

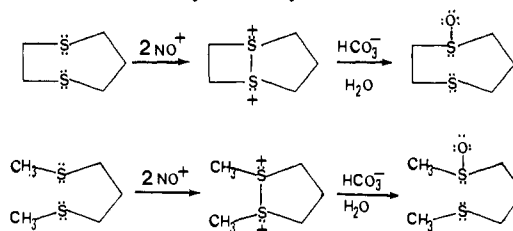
1,5-DTCO dication behaves as an electrophile on treatment with a saturated aqueous solution of sodium bicarbonate to give 1,5-DTCO monosulfoxide in 80% yield. Since this reaction gives the best yield of a characterizable product, all the dicationic species were treated with aqueous bicarbonate as soon as 90% or more of the nitric oxide was evolved. For example, when 1,4-DTCH is treated with 2 equiv of nitrosyl hexafluorophosphate in dry propionitrile, 90% of the expected nitric

Table II. Results of Synthesis of Monosulfoxides of Dithioethers

dithioether	isolated yields of monosulfoxide, %	dithioether	isolated yields of monosulfoxide, %
1,4-DT ^a	60	1,6-DTCD ^b	85
1,4-DTCH	74	2,5-DTH	71
1,4-DTCO	72	2,6-DTHP	84
1,5-DTCO ^b	80	2,7-DTO	70
1,5-DTCN ^b	80		

^a Only 80% nitric oxide evolved. ^b Also formed by reaction of solid dications with saturated sodium bicarbonate solution.

oxide is evolved. The propionitrile solution is then added to an aqueous saturated sodium bicarbonate solution. The reaction product is extracted into chloroform to give pure 1,4-DTCH monosulfoxide in 74% yield. Acyclic dithioethers react in a



similar manner. The results of this reaction for all the dithioethers are summarized in Table II.

To demonstrate the formation of dithioether dications in other reactions, we recently reported that the reduction of both 1,5-DTCO and 2,6-DTH monosulfoxides with iodide in aqueous solution proceeds extremely rapidly via a dicationic intermediate. Since the reaction is reversible, the oxidation of these dithioethers with triiodide also proceeds via the same dicationic intermediate.²¹

Since one- and two-electron oxidations by chemical oxidants occur readily for the dithioethers, an electrochemical study was initiated. In collaboration with R. Glass and G. Wilson (University of Arizona) the cyclic voltammetry of the dithioethers in acetonitrile was studied.²² 1,5-DTCO, 1,5-DTCN, and 1,6-DTCD show reversible oxidations. The peak potential of 1,5-DTCD is 0.343 V.

The implications of the existence and stability of dithioether cation radicals and dications is profound in that it suggests that neighboring thioether groups as well as other lone pair donors facilitate electron transfer processes. Glass and Wilson²³ recently reported that neighboring carboxylate and hydroxyl groups facilitate the oxidation of thioethers. Stein and Taube²⁴ have recently shown that a transannular sulfur-sulfur interaction occurs in $[\text{Ru}(\text{NH}_3)_5(1,5\text{-DTCO})]^{3+}$ and in the dimeric mixed-valence complex $[(\text{Ru}(\text{NH}_3)_5)_2(1,5\text{-DTCO})]^{5+}$. The interaction in the dimer may provide an essentially adiabatic electron transfer between metal centers.²⁴ In addition, we reported²⁵ that the electron impact induced fragmentation of the series of mesocyclic dithioethers gives 1,2-dithiolane and 1,2-dithiane cation radicals when a transannular interaction results in the initial formation of five- or six-membered ring cation radicals. Such cooperativity in electron transfer processes by proximate nucleophiles may be extremely important in protein systems, where the protein conformation places an electron pair donor of one amino acid in the correct position to participate in electron transfer processes with a thioether group. If participation occurs, the role of the thioether group in biological systems may be far more important than previously believed.

Experimental Section

Physical Measurements. ESR spectra were determined on a Varian

Model E4 spectrometer. ^1H NMR spectra were measured on a Varian Model EM-360 spectrometer. ^{13}C NMR spectra were measured at 25.14 MHz on a Nicolet TT-23 spectrometer. Ultraviolet and visible spectra were determined on a Cary-17 recording spectrometer. Infrared spectra were measured on a Beckman IR8 or IR12 infrared spectrometer. Microanalyses were performed by the Microanalytical Laboratory, operated by the College of Chemistry, University of California, Berkeley, Calif.

Solvents. Acetonitrile, reagent (Mallinckrodt Chemical Works), was dried over Linde 3 Å molecular sieves and then distilled from thianthrene tetrafluoroborate prior to use. Propionitrile, 99% (Aldrich Chemical Co., Inc.), was dried over Linde 3 Å molecular sieves and then distilled from concentrated sulfuric acid or from thianthrene hexafluorophosphate and then stored on the vacuum line until ready for use.

Reagents. Most commercially available reagents were used without purification. Nitrosyl tetrafluoroborate (Aldrich Chemical Co., Inc.) was sublimed at 220°C under vacuum prior to use. Nitrosyl hexafluorophosphate (Ozark-Mahoning Chemical Co.) was sublimed at 250°C under vacuum prior to use.

Syntheses. 1,3-Propanedithiol. 1,3-Propanedithiol was synthesized by a modification of the method of Eastman and Kritchevsky.²⁶

1,4-Butanedithiol. 1,4-Butanedithiol was synthesized by a modification of the procedure of Speziale.²⁷

1,4-Dithiacycloheptane. 1,4-DTCH was prepared using a method similar to that of Tucker and Reid.²⁸

1,4-Dithiacyclooctane. Into a three-neck 2-L Morton flask fitted with an overhead stirrer, condenser, and adaptor for a syringe pump was placed 700 mL of absolute ethanol. With rapid stirring, 12 g (0.52 g-atom) of freshly cut sodium was added under nitrogen. After all the sodium had reacted, the solution was heated to 50 °C and 30 mL (0.25 mol) of 1,4-dibromobutane and 21 mL (0.25 mol) of 1,2-ethanedithiol, each diluted to 50 mL with absolute ethanol, were added simultaneously by a syringe pump at a rate of 0.15 mL/min. The resulting solution was concentrated under vacuum to a thick, oily residue, water was added, and the mixture was extracted three times with dichloromethane. The combined organic phase was dried over Na_2SO_4 , filtered, concentrated, and distilled under vacuum to give 2.74 g (7.4%) of 1,4-DTCO: bp 47–48 °C (3 mm); ^1H NMR (CCl_4) δ 3.1 (m, 4, $-\text{CH}_2\text{S}$), 2.9 (s, 4, $-\text{CH}_2\text{S}$), 2.0 (m, 4, $-\text{CH}_2-$); ^{13}C NMR (CDCl_3) δ 33.7, 31.4, 25.8.

1,5-Dithiacyclooctane. 1,5-DTCO was synthesized by a modification of the procedure of Meadow and Reid²⁹ and Leonard, Milligan, and Brown.³⁰

1,5-Dithiacyclononane. Into a three-neck 2-L Morton flask fitted with overhead stirrer, condenser, and adaptor for syringe pump was placed 1200 mL of absolute ethanol. With rapid stirring 12 g (0.52 g-atom) of freshly cut sodium was added under nitrogen. After all the sodium had reacted, the solution was heated to 50 °C and 30 mL (0.25 mol) of 1,4-dibromobutane and 25.1 mL (0.25 mol) of 1,3-propanedithiol, each diluted to 50 mL with absolute ethanol, were added simultaneously by a syringe pump at a rate of 0.15 mL/min. The resulting yellow solution was refluxed for 1.5 h and then concentrated under vacuum. Water was added to the resulting white solid and yellow oil, and the mixture was extracted three times with dichloromethane. The combined organic phase was dried over Na_2SO_4 , filtered, and concentrated under vacuum. Distillation gave 2.35 g (5.8%) of 1,5-DTCN: bp 78–80 °C (0.6 mm); mp 58.5–60.0 °C (lit.¹² mp 58.5–59.5 °C); ^1H NMR (CCl_4) δ 2.9 (m, 4, $-\text{CH}_2\text{S}$), 2.7 (m, 4, $-\text{CH}_2\text{S}$), 2.0 (m, 4, $-\text{CH}_2-$), 1.8 (m, 2, $-\text{CH}_2-$); ^{13}C NMR (CDCl_3) δ 32.2 (double intensity), 28.9 (double intensity), 26.0 (double intensity), 21.8.

1,6-Dithiacyclodecane. 1,6-DTCD was synthesized by a modification of the procedure of Ochrymowicz, Mak, and Michna.³¹

2,6-Dithiaheptane. 2,6-DTHP was synthesized by a modification of the procedure of Protiva, Jilek, and Exner³² and of Jerchel, Dipplhofer, and Renner.³³

2,7-Dithiaoctane. 2,7-DTO was synthesized in a manner identical with that of 2,6-DTHP.

1,5-DTCO Dication. Into a small flask was placed 0.326 g (2.2 mmol) of 1,5-DTCO. The flask was connected to the reaction tube containing 0.517 g (4.4 mmol) of nitrosyl tetrafluoroborate. Then 15 mL of acetonitrile was added to both the flask containing 1,5-DTCO and the tube containing nitrosyl tetrafluoroborate, and the apparatus was connected to a vacuum line. The mixtures were frozen and degassed several times to remove any noncondensables. The mixtures

were allowed to come to room temperature, and the 1,5-DTCO solution was added to the nitrosyl tetrafluoroborate. The solution became yellow and then clear and colorless and a white precipitate formed. The evolved nitric oxide was measured and found to be 4.3 mmol (98%). The reaction flask was removed from the vacuum line and opened in a drybox under a nitrogen atmosphere. The clear, colorless solution and white solid were transferred to a clean, dry tube and a few milliliters of dry diethyl ether was added to cause further precipitation. After the precipitate had settled the remaining solvent was pipetted off and placed into another clean tube. Both tubes were then reconnected to the vacuum line. The white solid was dried under vacuum overnight. The resulting solution was fractionally crystallized to give more white solid: UV_{max} (CH_3CN) 233 nm (ϵ 9.6×10^3), 212 (3.8×10^3); ^{13}C NMR (CD_3CN) δ 53.0 (double intensity), 35.0.

Anal. Calcd for $\text{C}_6\text{H}_{12}\text{B}_2\text{F}_8\text{S}_2$: C, 22.39; H, 3.76. Found: C, 22.61; H, 3.87.

1,5-DTCN Dication. 1,5-DTCN dication was synthesized in a manner identical with that of 1,5-DTCO dication: UV_{max} (CH_3CN) 237 nm (ϵ 6.9×10^3); ^{13}C NMR (CD_3CN) δ 51.4 (double intensity), 38.5 (double intensity), 33.5 14.4 (double intensity).

Anal. Calcd for $\text{C}_7\text{H}_{14}\text{B}_2\text{F}_8\text{S}_2$: C, 25.0; H, 4.2. Found: C, 25.3; H, 4.4.

1,6-DTCD Dication. 1,6-DTCD dication was synthesized in a manner identical with that of 1,5-DTCO dication: UV_{max} (CH_3CN) 232 nm (ϵ 3.7×10^3); ^{13}C NMR (CD_3CN) δ 36.7, 16.8.

Anal. Calcd for $\text{C}_8\text{H}_{16}\text{B}_2\text{F}_8\text{S}_2$: C, 27.46; H, 4.61. Found: C, 27.67; H, 4.72.

(1,5-DTCO)PF₆. Into a small flask was placed 0.158 g (1.07 mmol) of 1,5-DTCO. The flask was connected to the reaction tube containing 0.187 g (1.07 mmol) of nitrosyl hexafluorophosphate, and the apparatus was placed on a vacuum line. Then 3.5 mL of propionitrile was condensed into the flask and reaction tube. The solutions were allowed to come to room temperature, and the 1,5-DTCO solution was added slowly to the nitrosyl hexafluorophosphate solution. The solution became deep red, and a red solid precipitated. The evolved nitric oxide was measured and found to be 1.04 mmol (97%). In a drybox the red solid was transferred to a vial and the sample was dried under vacuum overnight. The red solid was dissolved in acetonitrile to give a red solution which became yellow in about 20 min at approximately 30 °C, visible ($\text{CH}_3\text{CH}_2\text{CN}$) λ_{max} 405 nm.

Anal. Calcd for $\text{C}_6\text{H}_{12}\text{F}_6\text{PS}_2$: C, 24.57; H, 4.12. Found: C, 24.50; H, 4.22.

Reaction of 1,5-DTCO Dication with Isopropyl Alcohol. Into a flask containing 2 mL of acetonitrile were added 16.3 mg (0.27 mmol) of isopropyl alcohol, 54.8 mg (0.29 mmol) of 2,6-di-*tert*-butylpyridine, and 14.0 mg (0.11 mmol) of nonane. 1,5-DTCO dication (42.5 mg, 0.14 mmol), prepared as described, was dissolved in 2 mL of acetonitrile under argon and stirred vigorously. The solution containing isopropyl alcohol was added by syringe. Aliquots were removed at various intervals and analyzed by gas chromatography (3 ft \times $\frac{1}{4}$ in. column of 20% Carbowax 20M on Chromosorb W, oven temperature 30 °C at a helium flow rate of 45 mL/min) for acetone and unreacted isopropyl alcohol. A 49% yield of acetone was obtained based on the area of the peaks due to acetone and the standard, nonane.

Sulfoxide Formation by Reaction of 1,4-DT with 2 Equiv of NOBF₄. Into a reaction tube were placed 0.22 g (1.90 mmol) of nitrosyl tetrafluoroborate and 0.11 g (0.95 mol) of 1,4-DT. The tube was rapidly cooled in liquid nitrogen and attached to the vacuum line. The solids were degassed and 14 mL propionitrile was condensed into the tube. The mixture was allowed to come to room temperature and stirred for 24 h, at which time 1.56 mmol (82%) of nitric oxide had been evolved. The resulting yellow solution was added to an aqueous saturated sodium bicarbonate solution. The mixture was extracted three times with chloroform. The combined organic layer was dried over Na_2SO_4 , filtered, and concentrated under vacuum to give a mixture of 1,4-DT and 1,4-DT monosulfoxide. 1,4-DT was recrystallized from ethanol, leaving 0.08 g (60%) of 1,4-DT monosulfoxide.

1,5-DTCN Monosulfoxide. Into a 250-mL flask with side arm fitted with rubber septum was added 2.19 g (18.7 mmol) of nitrosyl tetrafluoroborate. The reaction flask was placed on a vacuum line and acetonitrile was condensed into the flask. A solution of 1.43 g (8.84 mmol) of 1,5-DTCN in acetonitrile was added through the septum cap by syringe. When the solution became clear and colorless and no more gas was evolved, the reaction flask was removed from the vacuum line and aqueous saturated sodium bicarbonate solution was added. The mixture was extracted three times with chloroform. The combined

organic phase was dried over Na_2SO_4 , filtered, and concentrated under vacuum to give 1.26 g (80%) of 1,5-DTCN monosulfoxide: mp 67–70 °C; IR (Nujol) 1010 cm^{-1} (S → O); $^1\text{H NMR}$ (CDCl_3) δ 3.2 (m, 4, $-\text{CH}_2\text{SO}$), 2.7 (m, 4, $-\text{CH}_2\text{S}$), 2.0 (m, 6, $-\text{CH}_2-$); $^{13}\text{C NMR}$ (CDCl_3) δ 47.8, 46.5, 31.8, 29.4, 26.5, 19.3, 17.4; mass spectrum (70 eV) *m/e* (rel intensity) 162 (53), 161 (21), 120 (31), 88 (60), 87 (93), 55 (100).

Anal. Calcd for $\text{C}_7\text{H}_{14}\text{OS}_2$: C, 47.15; H, 7.91. Found: C, 46.92; H, 7.66.

2,6-DTHP Monosulfoxide from 2,6-DTHP Dication. Into a small flask was placed 0.287 g (2.1 mmol) of 2,6-DTHP. The flask was connected to the reaction tube containing 0.738 g (4.2 mmol) of nitrosyl hexafluorophosphate. The apparatus was connected to a vacuum line and degassed. Dry propionitrile (10 mL) was condensed into both the flask of 2,6-DTHP and the tube of nitrosyl hexafluorophosphate. The solutions were allowed to come to room temperature and then cooled to 0 °C in an ice-water bath. The 2,6-DTHP in propionitrile was added slowly (by rotating the flask) to the rapidly stirring solution of nitrosyl hexafluorophosphate in propionitrile. The solution became a red-brown color immediately on mixing and bubbled vigorously as the nitric oxide was evolved. After all the 2,6-DTHP had been added, the solution became pale yellow and then clear and colorless. The evolved nitric oxide was measured and found to be 3.9 mmol (93%). The reaction flask was removed from the vacuum line, and the solution was poured into a saturated aqueous sodium bicarbonate solution. The resulting mixture was extracted three times with chloroform. The combined organic phase was dried over Na_2SO_4 , filtered, and concentrated under vacuum to give 0.269 g (84%) 2,6-DTHP monosulfoxide. Yields for all of the other monosulfoxides synthesized by this method are in Table II.

Acknowledgment. We wish to thank the University of California for a Faculty Research Grant and the Eastman Kodak Co. for a fellowship to Patricia B. Roush.

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Reactivity in Methyl Transfer Reactions.¹ 2. Leaving Group Effect on Rates with Substituted Thiophenoxides

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Abstract: Rates are reported for the reaction of various methylating agents (CH_3X) with the *p*-nitrophenoxide ion and several substituted thiophenoxides in sulfolane solution. The leaving groups, X, in increasing order of rate with thiophenoxide ion are O_3SCH_3 , *p*- $\text{O}_3\text{SC}_6\text{H}_4\text{CH}_3$, O_3SOCH_3 , I, O_3SF , O_3SCF_3 , $^+\text{O}(\text{CH}_3)_2$. The rates vary from 10^2 to more than $10^8\text{ M}^{-1}\text{ s}^{-1}$ in this series. With substituted thiophenoxides methyl tosylate and methyl iodide show identical substituent effects, but methyl trifluoromethanesulfonate is slightly but significantly less sensitive to substituents. Trimethyloxonium ion is even less selective, but the rate is approaching the diffusion limitation. The preparatively useful reaction of methyl triflate with phenoxide ion in ethanol solution emphasizes the persistence of considerable selectivity even with very reactive reagents.

Organic chemists have learned to expect very reactive reagents to be rather indiscriminate, and this expectation is now virtually an article of faith. The concept, dating from the early considerations of Polanyi,² has been variously restated and updated from qualitative, quantitative, empirical, and theoretical aspects.³ Nevertheless, the concept has been questioned

and counterexamples have been found, for example the work of Ritchie⁴ and the extensive review of Johnson.⁵

The reactivities of arylated nucleophiles toward methylating agents CH_3X might be described by the Hammett equation, the Swain-Scott equation,⁶ or even the Ritchie equation,⁴ although these nucleophiles are not generally listed with ap-